

Corrosion Inhibition of Cu-37Zn and Cu-10Ni Alloys in Simulated Sea Water Using Benzotriazole

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Abstract

This paper investigates the effect of benzotriazole (BTAH) on the corrosion of Cu-37Zn and Cu-10Ni alloys in 3.5% NaCl solution contaminated and non-contaminated with sulfide ions. Potentiodynamic polarization, potentiostatic polarization and polarization resistance measurements were performed in this investigation. At lower concentration of BTAH (0.001 M) Cu-37Zn exhibited slightly better behavior than Cu-10Ni while at high concentration (≥ 0.005 M) the Cu-10Ni alloy showed excellent inhibition efficiency. The contamination of sea water by sulfide ions diminished the protection afforded by BTAH for both alloys.

Keywords

Brass; Cu-Ni; Polarization; Corrosion; Inhibition; Benzotriazole; SEM

Introduction

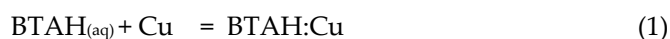
Brass corrosion has been much investigated in chloride solution by many authors [N. Bellakhal et al (2004); Antonijević et al (2005); Abd El Rehim, et al (1995); Fenelon and Breslin (2001); Quraishi, et al (2000); Martin, et al (2000)]. Abd El Rehim et al. (1995) investigated electrochemical behavior of brass in aerated NaCl solution. Results showed that at more negative potentials, Zn dissolution occurs while above a critical potential simultaneous dissolution of both copper and zinc occurs. Fenelon and Breslin (2001) have investigated electrochemical behavior of Cu, Cu-37Zn and Zn in chloride solutions containing BTAH, and found that BTAH causes inhibition of CuCl_2 formation as well as formation of a product rich in Zn. Quraishi et al. (2000) postulated 90–95% inhibiting efficiency of aminoalkyl mercaptotriazoles on brass 70/30 tested in 3% NaCl solution. Martin et al. (2000) investigated brass dissolution in a 0.5 mol dm^{-3} NaCl solution, clearly observing two separate regions, the first of which is unstable, obtained by dissolution of

Zn and formation of vacancies, and the other with stable and rich copper surface.

Cu–Ni alloys have tremendous applications in different industries, especially in ships, power stations and heat exchangers where chloride containing waters are almost used. The understanding of the corrosion processes under the influence of chloride ions and the control of these processes was the subject of intensive investigations [Badawy et al. (2006); Milosev et al. (1997); Kamkin et al. (1999); Blundy and Pryor (1972); Badawy et al. (2005)]. In solutions with chloride concentration higher than 0.5 M, a relatively high nickel content is needed to combat the corrosion process. Alloys with more than 50% Ni have shown lower corrosion currents compared to pure Cu [Milosev et al. (1997); Kamkin et al. (1999)]. The increase of Ni content is usually expensive and leads to the selective removal of Ni, especially in chloride containing solutions [Blundy and Pryor (1972); Badawy et al. (2005)]. The use of inhibitors seems to be the best way to overcome the corrosion problems of the Cu–Ni alloys of low Ni contents.

Benzotriazole (BTAH) has long been known as an efficient inhibitor for the corrosion of copper and its alloys [Zhang et al (2006); Allam et al (2006); Chieb et al (2011)]. Early studies suggested that the cuprous oxide was essential for the formation of the CuBTA film. By contrast, Zhang et al (2006) claimed that CuBTA film has been also formed on oxide-free copper surface.

Two mechanisms have been proposed to account for benzotriazole (BTAH) high inhibiting efficiency. The first attributes it to the adsorption of benzotriazole on the copper surface [Allam et al (2006)] i.e.



where BTAH:Cu refers to BTAH adsorbed on the copper surface. The second mechanism postulates the formation of a polymeric complex of Cu(I)BTA,



Youda et al. (1990) suggested that adsorption and complex formation are in equilibrium, i.e.



Eq. (3) reveals that the rise of the pH value contributes to the increment of the potential in the noble direction or the inhibitor concentration which favors the formation of the protective polymeric film. On the other hand, benzotriazole inhibition efficiency is lowered when the medium is contaminated with sulfide ions [Al Kharafi et al (2007); Allam et al (2007); Allam and Ashour (2008); Boyapati and Kanukula (2013); Khadom (2013)].

The present work aims to investigate and compare the corrosion inhibition effect of benzotriazole on Cu-37Zn and Cu-10Ni alloys in sea water. It also addresses the effect of sulfide pollution on the performance of benzotriazole. To our best knowledge, there is plenty work on copper whereas little attention has been paid to brass and copper-nickel alloys.

Experimental

Electrodes were prepared from brass (Cu-37Zn) and Cu-10Ni as the testing specimens. The electrodes were in the form of rods having 0.96 cm diameter (i.e. 0.7234 cm² cross sectional area). The immersed length of the rod was coated with a protective adhesive so that only the cross sectional area is exposed to the solution. Electrical contact to the external circuit is made through the rod. Electrodes were polished using SiC papers successively up to 2400 grits, followed by 0.3 micron alumina to acquire a mirror-like finish. A conventional three-electrode cell was used with an Ag/AgCl reference electrode (0.197 V SHE) and a platinum counter electrode. Solutions were prepared using deionized water, benzotriazole (BTAH) from Aldrich, NaCl and Na₂S from Fluka. Potentiodynamic polarization curves were measured (at 5 mV s⁻¹ scan rate) in 3.5% NaCl in the absence and presence of different concentrations of BTAH and/or Na₂S. The potential was controlled using a computerized potentiostat (Autolab PG STAT). Potential scanning started from the less to the more noble potentials. Measurements were performed at 25±1°C while the electrolyte was stirred using a magnetic stirrer. The electrodes were preimmersed for 15 min in the testing solution before the polarization curves were measured

for steady state. From the potentiodynamic curves, a certain potential was selected (in the passive region) and specimens of the tested alloys were potentiostatically polarized to this potential and kept at this potential for 2 hours. Polarization resistance (*R_p*) was determined using electrochemical impedance spectroscopy (EIS) technique. EIS measurements were carried out under the open circuit potential within a frequency ranging from 100 kHz to 0.1 Hz. The amplitude of the sinusoidal voltage signed was 5 mV.

Results and Discussions

Potentiodynamic Polarization

Figures 1&2 show the potentiodynamic polarization curves of Cu-37Zn and Cu-10Ni alloys tested in 3.5% NaCl in the presence and absence of different concentrations of BTAH. In the absence of BTAH, the Cu-10Ni alloy shows a slightly better resistance than Cu-37Zn alloy. *E_{corr}* of the Cu-10Ni alloy is slightly higher than the Cu-37Zn alloy while the limiting current shows more noble value. The addition of BTAH results in a marked effect on the polarization curves of both alloys. In case of Cu-37Zn alloy, the addition of BTAH results in the development of a passive region of about 0.3 V for 0.001 M BTAH and 0.4V for 0.005 BTAH while 0.01 M BTAH gives a 0.5 V passive region. It is also noted that the addition of BTAH results in the shift of *E_{corr}* towards less noble values. In case of Cu-10Ni alloy, the addition of 0.001 M BTAH has no effect on the potentiodynamic polarization behavior of the alloy. On the other hand, the addition of either 0.005 or 0.01 M BTAH results in improving the corrosion resistance of the alloy to a very large extent. A quite large passive region is obtained (>1.0 V) with a passivation current of ~10⁻⁶ Acm⁻². *E_{corr}* values at both concentrations are shifted towards more noble values.

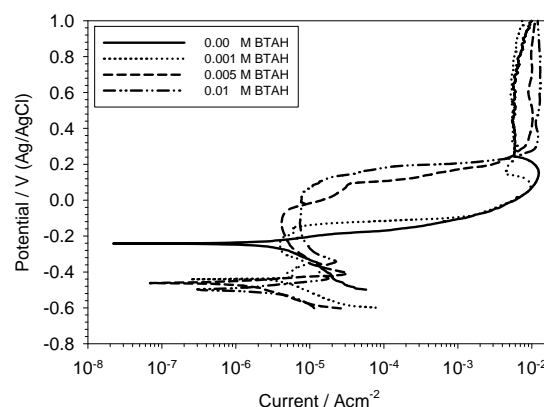


FIG. 1: EFFECT OF BTAH ON THE POTENTIODYNAMIC POLARIZATION CURVES OF Cu-37Zn ALLOY IN 3.5% NaCl AT 5 mV s⁻¹ VOLTAGE SCAN RATE AND 25°C.

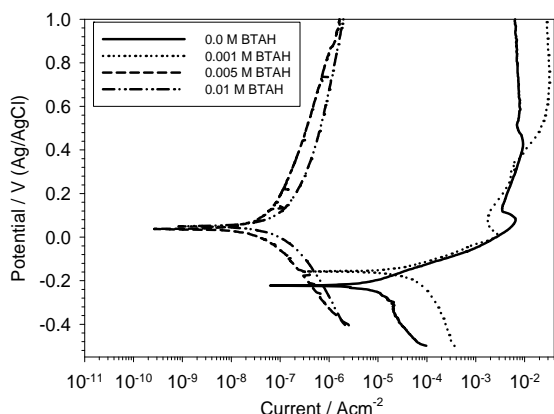


FIG. 2: EFFECT OF BTAH ON THE POTENTIODYNAMIC POLARIZATION CURVES OF Cu-10Ni ALLOY IN 3.5% NaCl AT 5 mV s⁻¹ VOLATGE SCAN RATE AND 25°C.

The degree of surface coverage at different concentrations of BTAH on both Cu-37Zn and Cu-10Ni can be obtained from the following expression:

$$\theta = \frac{I_{corr(b)} - I_{corr(inh)}}{I_{corr(b)}} \quad (4)$$

where $I_{corr(b)}$, $I_{corr(inh)}$ represent corrosion current densities in the absence and presence of the inhibitor. Table 1 contains the surface coverage values for different inhibitor concentrations that were determined from polarization curves in Figures 1&2. The interaction of BTAH with the surface of alloys was best described using the Langmuir isotherm. This isotherm is [El-Egamy (2008); Milic and Antonijevic (2009)]:

$$\frac{\theta}{1-\theta} = AC \exp\left(\frac{-E^\#}{RT}\right) = KC \quad (5)$$

where θ is the surface coverage, $E^\#$ is the activation energy, C is the concentration in mol L⁻¹ and K is the constant of the adsorption process. The above equation can be simplified as:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (6)$$

A plot of C/θ versus C yields a straight line with intercept $1/K$. Figure 3 shows the relationship between C/θ and C for the two investigated alloys. The relationship between the adsorption constant and the standard free energy of adsorption (ΔG°) is given by [Ehteshamzade et al (2006); Scendo (2007); Donahue and Nobe (1965)]:

$$K = \left(\frac{1}{55.55}\right) \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad (7)$$

where R is the universal gas constant and T is the absolute temperature. Standard free energy of adsorption (ΔG°) of -25.35 and -27.53 kJ mol⁻¹ were obtained for Cu-37Zn and Cu-10Ni, respectively. The value of ΔG° indicates the spontaneity of the adsorption reaction of BTAH on the surface of tested alloys [Kamis et al (1991); Khadom et al (2010)].

The effect of sulfide ions on the potentiodynamic polarization curves of Cu-37Zn and Cu-10Ni is illustrated in Figure 4 which shows the effect of addition of 0.001 M HS⁻ to the 3.5% NaCl solution containing 0.01 M BTAH on the polarization curves of tested copper alloys. The presence of sulfide ions, specifically for Cu-10Ni alloy, results in the shift of E_{corr} towards more negative values by hundreds of millivolts. It also increases the current by orders of magnitude.

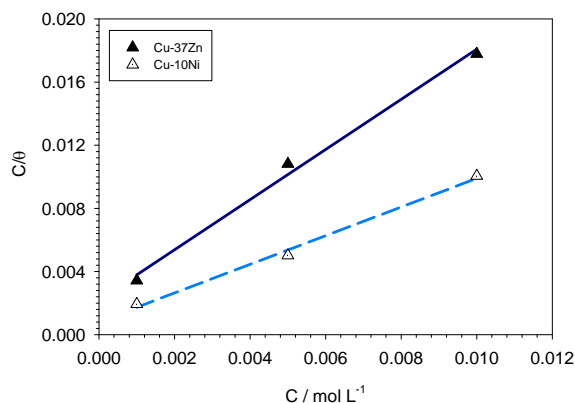


FIG. 3 LANGMUIR ADSORPTION ISOTHERMS OF Cu-37Zn AND Cu-10Ni ALLOYS IN 3.5% NaCl IN THE PRESENCE OF BTAH AT 25°C.

Potentiostatic Polarization

Figures 4&5 present the effect of addition of BTAH and injection of 10⁻³ M HS⁻ on the potentiostatic polarization curves of copper alloys treated in 3.5% NaCl at 0.0 V (Ag/AgCl). Part (a) of each curve shows the steady currents obtained in the salt solution in the absence of both BTAH and HS⁻ ions. Steady current values of about 0.002 and 0.001 A cm⁻² were obtained for Cu-37Zn and Cu-10Ni, respectively. The presence of 0.01 M BTAH decreases the current towards very small values that can be neglected, indicating the excellent inhibition efficiency of BTAH. Steady currents of 7.0×10⁻⁸ and 3.5×10⁻⁸ A cm⁻² were obtained for Cu-37Zn and Cu-10Ni, respectively (part (b) in each curve). However, upon injection of 0.001 M HS⁻, the current jumps towards values as high as 10⁻⁵ A cm⁻² (part (c) in each curve). The extent of current jump was slightly higher for Cu-37Zn than the Cu-10Ni. In spite

of the fact that sulfide injection predominantly increases the current, the steady currents obtained in the presence of BTAH are still quite low in comparison to those obtained in the absence of the inhibitor. The increase in current indicates that the inhibitive action of BTAH is lowered in the presence of sulfide ions.

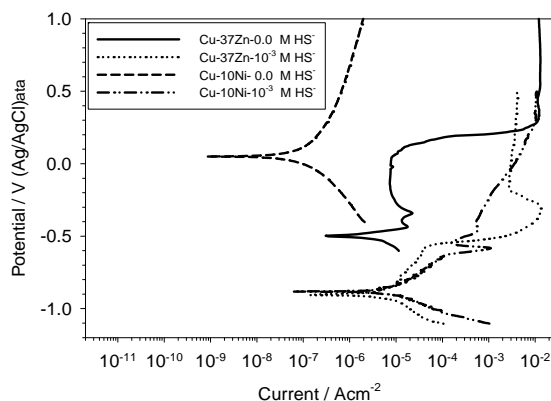


FIG. 4: EFFECT OF SULFIDE IONS ON THE POTENTIODYNAMIC POLARIZATION CURVES OF Cu-37Zn AND Cu-10Ni ALLOYS IN 3.5% NaCl SOLUTION CONTAINING 0.01 M BTAH AT 5 MV S⁻¹ SCAN RATE AND 25°C.

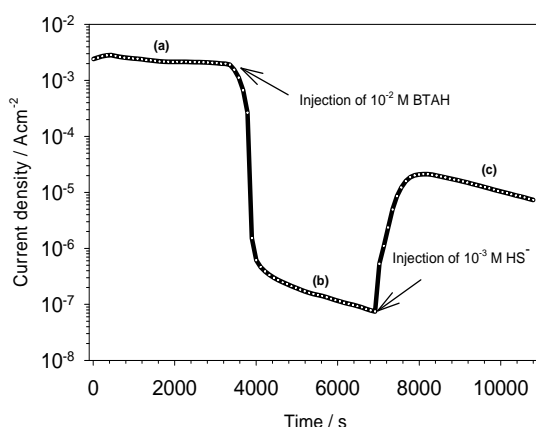


FIG. 5: EFFECT OF INJECTION OF BTAH AND SULFIDE IONS ON THE POTENTIOSTATIC POLARIZATION CURVES OF Cu-37Zn AND Cu-10Ni ALLOYS IN 3.5% NaCl AT 25°C AND 0.0 V (Ag/AgCl).

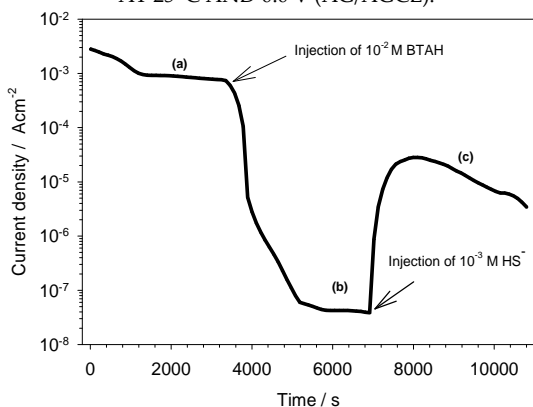


FIG.6: EFFECT OF INJECTION OF BTAH AND SULFIDE IONS ON THE POTENTIOSTATIC POLARIZATION CURVES OF Cu-37Zn AND Cu-10Ni ALLOYS IN 3.5% NaCl AT 25°C AND 0.0 V (Ag/AgCl).

Electrochemical Impedance Spectroscopy (EIS)

Polarization resistance of Cu-37Zn and Cu-10Ni alloys was determined in 3.5% NaCl in the absence and presence of different concentrations of BTAH using electrochemical impedance spectroscopy (EIS) technique. The polarization resistance (R_p), can be calculated by subtracting the impedance at the high frequency which represents the solution resistance (R_s) from the impedance at the low frequency which represents the $R_p + R_s$. This also can be done using the instrument software by fitting the data to an equivalent circuit predetermined in the software. Figs.6&7 show the EIS spectra of Cu-37Zn and Cu-90Ni alloys. R_p values calculated using these spectra are presented in Figure 8. The polarization resistance is inversely proportional to the corrosion current (i_{corr}) according to the stern-Geary relationship.

$$R_p = \beta_a \beta_c / 2.3 (\beta_a + \beta_c) i_{corr} \quad (4)$$

where β_a and β_c are the cathodic and anodic Tafel slopes. Equation 4 denotes that there is a direct proportionality between R_p and corrosion resistance. Figure 8 shows that the presence of BTAH leads to the increase of R_p for the tested alloys. However; the response differs from one alloy to another. The largest increase in R_p is exhibited for the Cu-10Ni alloy at 0.005 and 0.01 M BTAH (1.38×10^5 and 1.83×10^5 ohm, respectively). Cu-37Zn alloy shows R_p value of 2.074×10^4 and 2.576×10^4 ohm for the same concentrations of BTAH, respectively. R_p values shown by the Cu-37Zn are quite low in comparison to those obtained for the Cu-10Ni alloy. Results of polarization resistance measurements are in agree with those of potentiodynamic and potentiostatic measurements assigning the highest inhibition efficiency of the BTAH film formed on the surface of Cu-10Ni alloy.

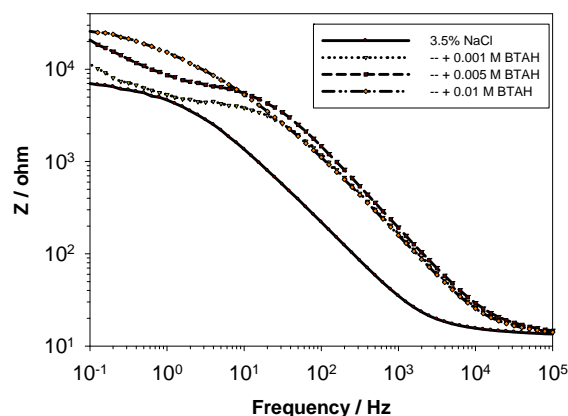


FIG. 7: EFFECT OF BENZOTRIAZOLE CONCENTRATION ON THE IMPEDANCE SPECTRA (BODE PLOT) OF Cu-37Zn TESTED IN 3.5% NaCl AT 25°C.

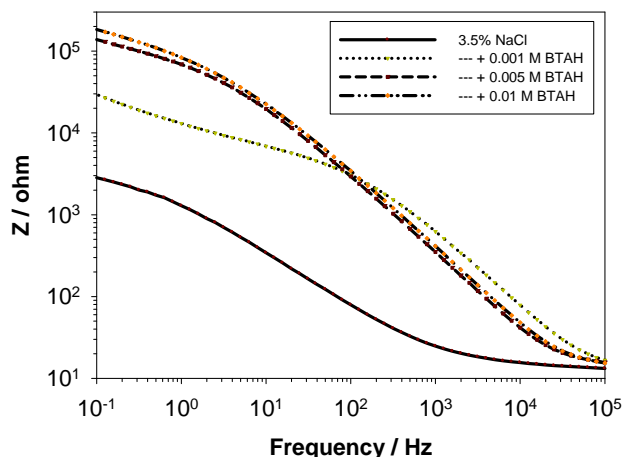


FIG. 8: EFFECT OF BENZOTRIAZOLE CONCENTRATION ON THE IMPEDANCE SPECTRA (BODE PLOT) OF Cu-10Ni ALLOY TESTED IN 3.5% NaCl AT 25°C.

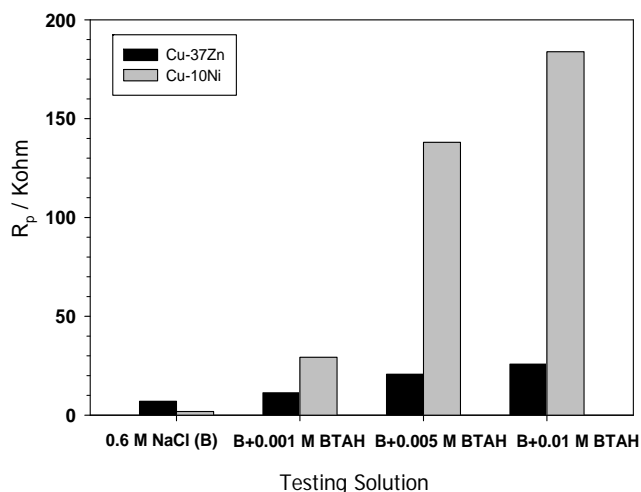
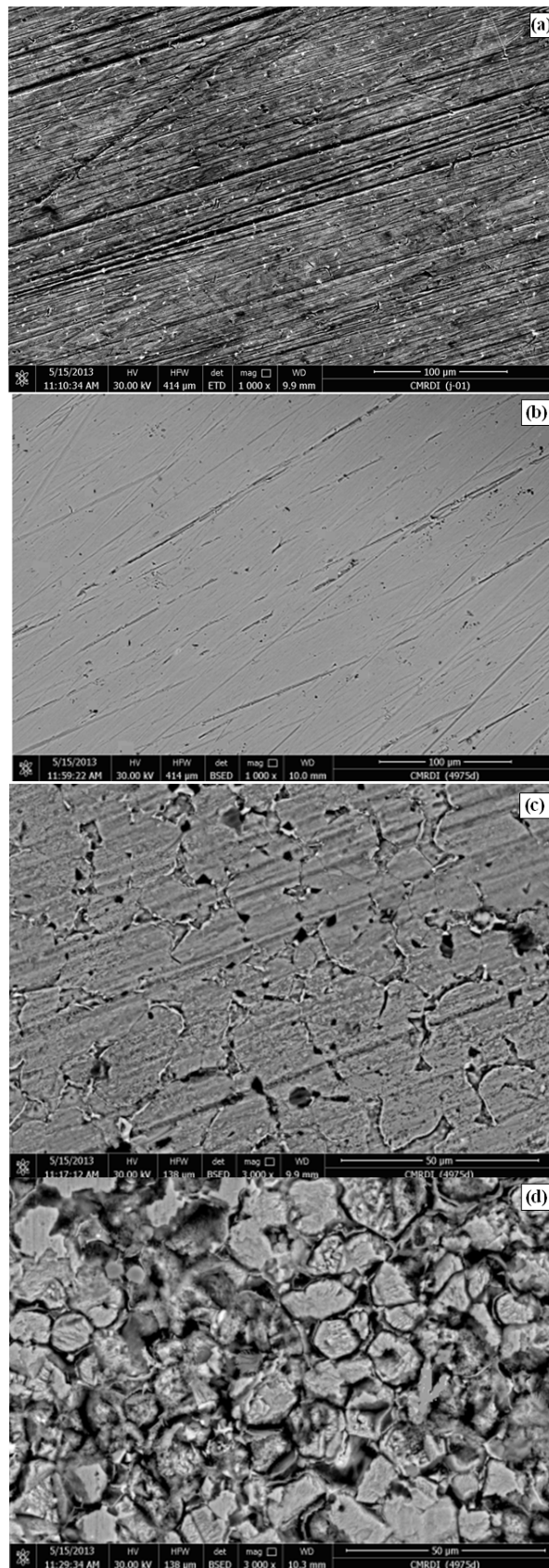


FIG.9: EFFECT OF THE CONCENTRATIONS OF BTAH ON THE POLARIZATION RESISTANCE (R_p) OF THE METAL/ELECTROLYTE INTERFACES OF ALLOYS TESTED IN 3.5% NaCl AT 25°C.

Surface Characterization

Figure 9 shows the scanning electron micrographs of Cu-37 and Cu-10Ni before and after corrosion testing in the absence and presence of sulfide ions. Image a and b represent the uncorroded surface for both alloys. It is seen that the Cu-37 Zn alloys is severely attacked in the sulfide contaminated salt water. The attack occurred on both the grain surface and the grain boundaries (image c). The presence of benzotriazole opposes the harmful effect of sulfide ions. The grain surfaces remained unattached while the grain boundaries attack was much weaker than that in the absence of BTAH. However; the presence of BTAH could not totally prevent the occurrence of intergranular corrosion (image d). On the other hand, Cu-10Ni alloy suffered much lower degree of

corrosion in comparison to the Cu-37Zn alloy with BTAH added or not (images e&f). No intergranular corrosion was seen on the alloy surface.



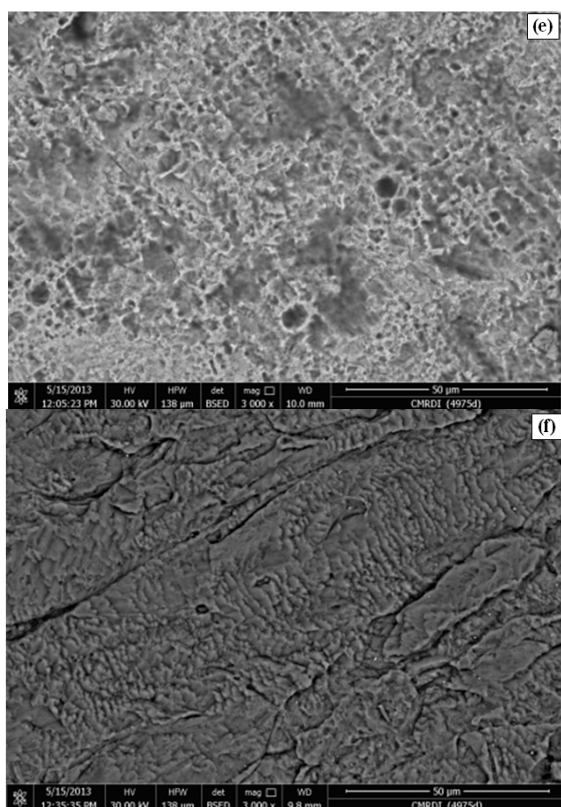


FIG. 10: SEM PHOTOGRAPHS OF Cu-37Zn AND Cu-10Ni ALLOYS; (A) & (B) REPRESENT THE UNCORRODED Cu-37Zn AND Cu-10Ni, REPECTIVELY; (C) AND (D) REPRESENTS THE SULPHIDE CORRODED Cu-37Zn ALLOY IN THE ABSENCE AND IN THE PRESENCE OF BTAH, REPECTIVELY; (E) AND (F) REPRESENTS THE SULPHIDE CORRODED Cu-10Ni ALLOY IN THE ABSENCE AND IN THE PRESENCE OF BTAH, REPECTIVELY.

The present work denotes an excellent corrosion inhibition of Cu-10Ni alloy compared to Cu-37Zn alloy at sufficiently high concentration of BTAH (≥ 0.005 M). All these observations can be understood if we look at the nature of the protective film formed on the surface of these alloys. It is well known that the resistance to seawater corrosion of copper and its alloys is related to the formation of a thin, adherent, protective surface film of cuprous oxide [Youda et al (1990)]. However, the formed film differs from one alloy to another. For Cu-37Zn alloy, the film contains ZnO in addition to the main constituent of Cu₂O [Kear et al (2004); Abouswa et al (2007); Antonijevic et al (2009)]. For Cu-10Ni alloy, nickel is incorporated in the Cu₂O film improving its characters and consequently results in the formation of a more protective copper benzotriazole film upon its presence in solution. It was also noted the shift of E_{corr} of Cu-37Zn alloy towards more negative values in the presence of BTAH. This can be related to the fact that

Zn in the Cu-37Zn alloy may be incorporated in the BTAH film [Zhou et al (2010)].

The loss of protection of benzotriazole in the presence of sulfide ions can be attributed to the very high stability of CuS in comparison to that of Cu(I)BTA complex [Dean (1992)]. Sulfide ions compete for Cu(I) ions under a much stronger driving force than BTAH and can extract the Cu(I) ions from the Cu(I)BTA complex [Aashour et al (2000); Al Kharafi et al (2007)]. Consequently, the protective Cu(I)BTA breaks down and corrosion occurs on the bare surface. There was no noticeable difference between the corrosion behavior of Cu-37Zn and Cu-10Ni alloys in the presence of sulfide ions. This can be understood knowing that the surface composition of these alloys is formed mainly from Cu₂O and hence the effect of sulfide addition would be the same.

Conclusions

Cu-37Zn and Cu-10Ni alloys were tested in sea water in the absence and presence of different concentrations of BTAH. At sufficiently high concentration (≥ 0.005 M) of BTAH, the Cu-10Ni alloy showed excellent inhibition efficiency compared to Cu-37Zn. EIS showed that the polarization resistance, R_p , and hence the corrosion resistance is increased with the increment of the concentration of BTAH. The excellent inhibition efficiency shown by Cu-10Ni can be related to the incorporation of nickel in the oxide film formed on the alloy surface improving its characteristics. BTAH loses its protection when sea water is contaminated by sulfide ions because the stability of CuS is much higher than that of Cu(I)BTA.

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